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DETERMINATION OF RARE EARTH ELEMENTS IN URANIUM COMPOUNDS

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DETERMINATION OF RARE EARTH ELEMENTS IN URANIUM COMPOUNDS

By R. C. Hirt and N. H. Nachtrieb

ABSTRACT

The separation of the "rare earth" elements from uranium and its compounds may be obtained by means of an ether extraction, precipitation as fluorides, and purification by way of the hydroxides. The final determination is carried out spectrographically, using a Jarrell-Ash Wadsworth Spectrograph and an A.R.L.-Dietert Multisource. Dysprosium, gadolinium, samarium, neodymium, praseodymium, lanthanum, and cerium were investigated, and their limits of sensitivity and their recoveries from U_3O_8 determined. The method may be applied to other "rare earth" elements as well.

The procedure used for the separation of the rare earth elements from uranium compounds was that given by H. G. Short and W. L. Dutton in BM - 325, with certain modifications to obtain more thorough separations. Greater sensitivities were obtained by use of a condensed discharge from an A.R.L.-Dietert Multisource instead of a DC arc, and by use of a Dietert Projection-Comparator Densitometer for measuring the relative transmissions of the lines from samples and those of a standard plate.

SPECTROGRAPHIC DETERMINATION OF RARE EARTH ELEMENTS

The spectrographic determinations were carried out with a Jarrel-Ash Wadsworth Automatic Spectrograph having a dispersion of 5.27 Å/mm. The electrodes were placed 45 cm from the slit, with a 90 mm spherical quartz lens 37 cm from the slit. The slit opening was 35 microns wide and 2 mm high. Eastman Spectrum-Analysis No. 1 plates were used for photographing the region from 2100 Å to 4800 Å.

Standard solutions of Dy, Gd, Sm, Nd, Pr, La, and Ce of a concentration of 100 micrograms/ml were prepared. These solutions were diluted to make standard solutions of concentrations of 10γ /ml and 1γ /ml. Suitable amounts of these solutions were evaporated on 6 mm diameter copper electrodes, on a flat surface freshly cut by a lathe. These were made the bottom electrodes in the spark.

An A.R.L.-Dietert Multisource operating off a 230-volt AC line at 19 amperes (primary) was used. 60 microfarads of capacity, 25 microhenries of inductance, and 25 ohms of resistance were introduced in the spark circuit. The spark operated at 920 volts, with a 10,000 volt initiator. Exposures were for 40 seconds. The resulting spark was found to be quite stable, and the exposure reproducible.

The S.A. No. 1 plates were developed in Eastman D-19 developer for 3 minutes, placed in an acetic acid short-stop bath for 10 seconds, and fixed in an Agfa acid hypo bath for 3 minutes. The plates were dried in a stream of warm air.

A standard plate was made up using 5, 2, 1, .5, .2, .1, .05, .02, .01, and .005 micrograms of each element. The selected lines were photometered on an A.R.L.-Dietert Projection-Comparator Densitometer, and the percentage-transmission vs quantity curves plotted. The plates from samples were treated in the same way, and the measured transmissions compared with the graph from the standard plate to determine the amount of the element in question that was present in the sample.

SENSITIVITIES

The limit of detectability for each rare earth element tested is given in Table 1.

Table 1.

Element	Limit of Detectability	
	Micrograms	Parts per million (10 gm sample)
Dy	.05	.005
Gd	.05	.005
Sm	.50	.050
Nd	.20	.020
Pr	.10	.010
La	.01	.001
Ce	.10	.010

CHEMICAL SEPARATIONS

a. The procedure given below is essentially that developed by Short and Dutton in BM-325. Advantage is taken of the solubility of uranyl nitrate in ether to separate the bulk of the uranium from the rare earth elements. The rare earths are precipitated as fluorides, and purified again by a precipitation as hydroxides to remove Al, Mg, and the last traces of uranium. Details of procedure are not given here; see BM-325.

b. Modifications of method of BM-325

1) Three ether-water extractions in place of two.

2) Fluoride precipitate after ignition twice treated with hot concentrated H_2SO_4 .

3) Several rinsings (as many as 5 or 6) of the precipitated hydroxides with 5% NH_4OH , found necessary to remove last traces of uranium to prevent the uranium lines ("background") from obscuring rare earth lines. Rinsings carried out until no yellow color could be detected on filter paper.

4) If multiple rinsings failed to remove yellow color, the precipitate was redissolved in HCl , and another precipitation of hydroxides carried out.

WAVELENGTHS USED FOR ANALYSIS

Table 2 gives the various lines used in the spectrographic analysis, together with their limits of detectability and coincident lines. The lines listed which do not have as low a limit of detectability as the most sensitive lines are used as confirming lines and are also useful when larger amounts of the element are present.

RECOVERIES

Various known amounts of the rare earth elements were added to 10-gram samples of U_3O_8 . These samples were subjected to the separation procedure, and the rare earths analyzed spectrographically. Table 3 shows typical recoveries. All samples were 10-grams unless otherwise marked.

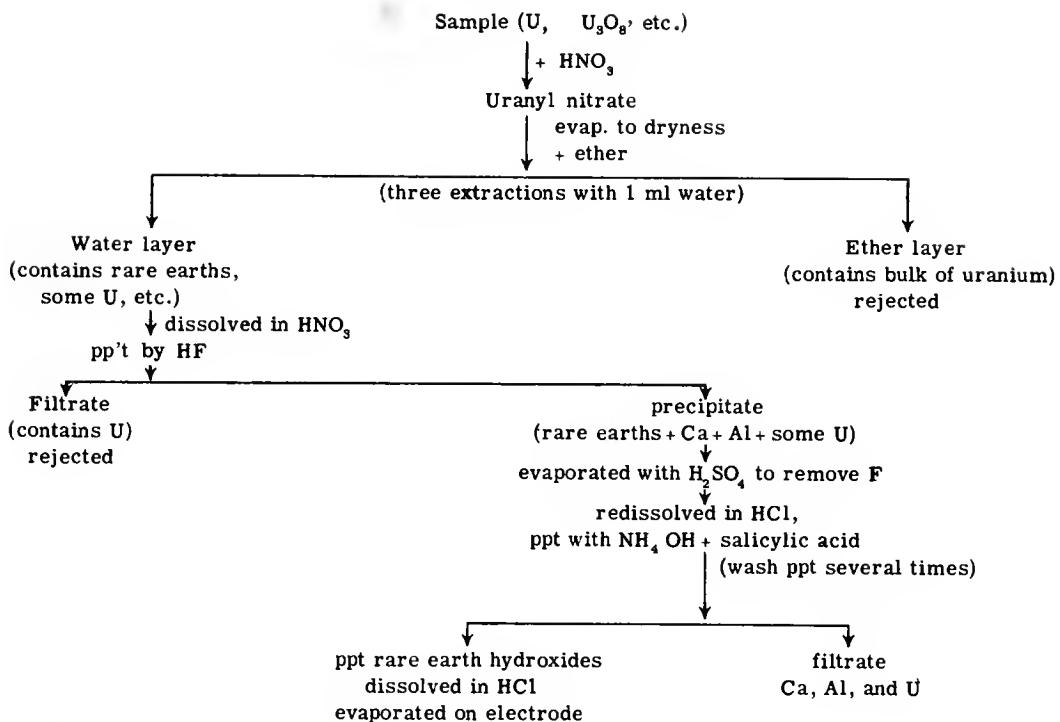


Table 3.

Element	Micrograms added	Micrograms recovered	Remarks
Dy	10	5 to 10	not accurate above 5 micrograms
	5	3 to 5	
	1	1	
	.5	.3 to .5	
Gd	10	5 to 10	not accurate above 5 micrograms
	5	4.5 to 5	
	1	1	
	.5	.4 to .5	
Sm	10	5 to 10	not accurate above 5 micrograms
	5	4.5 to 5	
	1	.8	
	.5	less than .6	limit of detectability .5
Nd	10	5 to 10	not accurate above 5 micrograms
	5	4 to 5	
	1	.7 to 1	
	.5	.3 to .5	
Pr	2	1.2 to 2	
Ce	2	1.5 to 2	
	1	.8 to 1	in 10 milligram sample
La	2	2	
	1	.7 to 1	in 10 milligram sample

Table 2.

Element	Wavelength	Detectability (micrograms)	Coincident Lines			
Dy	3531.71	.05	Er	3531.71	Mn	3531.85
	3577.99	.05	Mn	3577.88	V	3577.87
	3407.80	.05	Fe	3407.46	Ce	3407.60
			Pt	3408.13		
	3538.52	.10	V	3538.24	Th	3538.75
	3393.58	.20	Fe	3392.66	Cr	3392.98
			Cr	3393.84		
Gd	3422.47	.05	Fe	3422.66	Cr	3422.74
	3100.51	.05	Fe	3100.30	Fe	3100.67
	3362.24	.05	Ca	3361.92		
	3350.10	.10	Ca	3350.21		
	3481.82	.10	V	3482.19	Zr	3481.15
Sm	3592.59	.50	Nd	3592.59	Gd	3592.70
	3745.62	.50	Fe	3745.56	V	3745.80
	3634.27	.50	Pd	3634.70	Mo	3635.14
	4256.40	.50	Nd	4256.48		
	3568.26	.50	Lu	3567.84		
Nd	4012.25	.20	Eu	4011.68	Ce	4012.39
			Mo	4011.97		
	3851.75	.20	Pr	3851.62	Fe	3852.57
	4303.57	.50	Zr	4302.89		
	3863.41	.50	U	3863.40	Th	3863.39
Pr	4156.08	1.00	Mo	4155.58	Zr	4156.24
	4100.75	.10	La	4099.54	Cb	4100.92
			In	4101.77	Yt	4102.38
	4008.71	.10	Fe	4009.71	Ti	4008.93
	4179.42	.20	Cr	4179.26	Cu	4179.51
La	4118.48	.20	Fe	4118.55	Sm	4118.54
	4189.52	.50	Gd	4191.08	Fe	4191.44
	3949.11	.01	Fe	3948.78	Pr	3949.44
			Eu	3949.59	Fe	3949.96
	3988.52	.05	Yb	3987.99	Pr	3989.72
Ce	3871.63	.05	Fe	3871.75	Dy	3872.12
	3794.77	.10	Fe	3795.00	Gd	3796.39
	3790.82	.10	Ru	3790.51	Nd	3790.84
	4151.97	.10	La	4151.96	Cb	4152.58
	4012.39	.20	Nd	4012.25	Cr	4012.47
			Fe	4013.82		
	3801.53	.20	Sn	3801.00		
	4137.65	.50	Re	4136.45	Cb	4137.10
	4186.60	.50	Dy	4186.81	Fe	4187.04
			Gd	4184.25	Fe	4184.90

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